Rheological Properties of Polyvinylacetate: Compliance and Relaxation Spectrum

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Abstract: *The dynamic viscoelastic properties of Polyvinylacetate with molecular weight 83000g/mol (PVA 83K) were determined by using a Rheometer operated in the dynamic mode and 8 mm parallel plate over a wide range of temperature as a function of frequency. The measurements were performed successively in the parallel plate geometry using 8 mm plate instead of 25 mm. The glass plateau regime is clearly observed because we could measure PVA 83K sample successively under its glass temperature. The rheological properties of polydisperse PVA 83K were completely studied. The storage and loss compliance and the relaxation spectrum are evaluated.*

Keywords: Viscoelastic properties of Polyvinyacetate, Relaxation spectrum, Compliance.

1. INTRODUCTION

Rheology is concerned with the description of the mechanical properties of the various materials under the various deformation conditions. Polymer rheology is in its various aspects intimately entwined with molecular physics, continuum mechanics, and the processing of polymeric materials. At present, rheological investigations of polymers are processing at an enormously rapid rate, embracing a wide range of materials: biological objects, paste-like substances such as lubricants. The applied aspects of rheology are tied up with the development of new technological processes for the processing of plastics, elastomers and fibers [1]. The understanding of the relationship between the rheological properties of polymers and their molecular structure has considerably improved in the past few years with the interest of physicists in the matter and particularly with the development of molecular dynamics theories [2]. Besides, rheological measurements are used now as an analytical tool of polymer characterization [3-13].

In this work the rheological properties are investigated in details for a commercial PVA 83K.

2. EXPERIMENTAL SECTION

Polydisperse PVA 83K sample was prepared for the Rheological measurements. In the disc form with 8 mm diameter and 1 mm thickness by using a press mould without vacuum at 50˚C under 10 bar for 20 min. The preparation steps and conditions are summarized as follows:

Approximately 0.1 g of the polymer is placed in a Teflon frame of dimensions 8 mm diameter and 1 mm thickness. This Teflon frame is introduced between two Teflon plates and positioned between two metallic plates in the mould. The sample is positioned on the lower plate followed by lowering the upper plate until just contact the upper Teflon plate. The sample is heated with heat rate 10˚C/min. and pressed under 8-10 bar by lowering the upper piston for 20 min. The mould is cooled to 30 ˚C , followed by taking the sample out.

After preparation the sample for the measurement, the sample is placed on the lower plate of the ARES-Rheometer followed by lowering the stage until the sample just contacts the upper fixture completely. The ARES-Rheometer, consists of a test station, a furnace and liquid nitrogen controller. The test station contains the motor and transducer between which the sample to be tested is placed. The furnace is a forced convection enviromental chamber that encloses the sample. The gas temperature is controlled by two resistive heaters and the nitrogen gaseous is used during testing at or above room temperature. If test temperatures are below room temperature, liquid nitrogen is used. The temperature of the oven is maintained by a control loop that is closed around a platinum resistive thermometer.

The normal force of the instrument should be kept around zero and the actual gap size is read electronically to be around 1 mm. The measuring program is adjusted to measure the sample over a wide range of temperature from 25 ˚C up to 150 ˚C as a function of frequencies in parallel plate geometry and dry nitrogen atmosphere .The strain was kept inside the linear regime in the whole frequency range. The strain is applied to the sample and the resulting stress is measured by the transducer. The stress signal generated by the sample separated into two components; an elastic part which is in the phase with strain and a viscouse contribution which is 90˚ out of phase with the strain.

3. RESULTS AND DISCUSSION

The PVA83K sample was measured over a temperature range 25-150°C as a function of frequency. Different temperatures curves were shifted into single curve (Master curve) to a reference temperature T0 (25 °C)by means of the time-temperature superposition principle as proposed by Williams, Landel and Ferry (WLF) [8].

Three regimes are found in Figure 1 where the storage, J'(w) and loss, J'' (w) compliance have roughly the appearance of mirror image of those of G' (w) and G'' (w).

Since the rubber-like regime is the indication of the entanglements where the chains are entangled each other above a certain molecular weight that called critical molecular weight, Mc.

A discrete relaxation spectrum using a small number of modes is derived to describe the relaxation behaviour of monodisperse polystyrene melts. Attention is focused on keeping the physical meaning of the relaxation times. Therefore, molecular dynamics theories are used in the terminal, plateau and transition zones and in the case of entangled melts. The spectrum is divided into three parts corresponding to three assumed different relaxation mechanisms: Rouse mechanism at short times, modified Rouse for tube equilibration and reptation with tube fluctuation in the long time range. This description only requires the knowledge of a limited number of parameters, namely the molecular weight of the polymer under investigation, the scaling law for Newtonian viscosity, the plateau modulus and the molecular weight between entanglements. The method is sucessfully applied to entangled monodisperse polystyrene melts and enables the recovery of final spectra containing only a few relaxation modes.

If the viscoelastic (viscous and elastic at same time) behavior of the polymer is represented by a finite mechanical model, the decay of G(t) must at the end become exponential, proportional to e-t/τi where τ_i is the terminal relaxation time. The results of the extension in the number of elements in the Maxwell model without limit is a continuos spectrum that is called relaxation spectrum, H(T) (Fig. 2). The characteristic zones of the viscoelastic time scale are clearly apparent in H: the glassy zone to the left of the principle maximum, the transition zone where H drops steeply, the terminal zone where it approaches zero.

4. CONCLUSION

The rheological properties of PVA 83K are evaluated using an ARES Rheometer operated in the dynamic mode. The measurements were performed successively in 8 mm a parallel plate instead of 25 mm.

From the results obtaine, the viscoelastic properties of PVA could be studied with high accuracy. The storage and loss compliance and the relaxation spectrum are evaluated.

5. ACKNOWLEDGMENTS

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6. THE ABBREVIATIONS AND NOTATION:

PVA 83K: Polyvinylacetate with molecular weight 83000g/mol.

ω : the angular frequency

J' : the storage compliance

J'' : the loss compliance

J* : the complex compliance

G_i : the relaxation strength
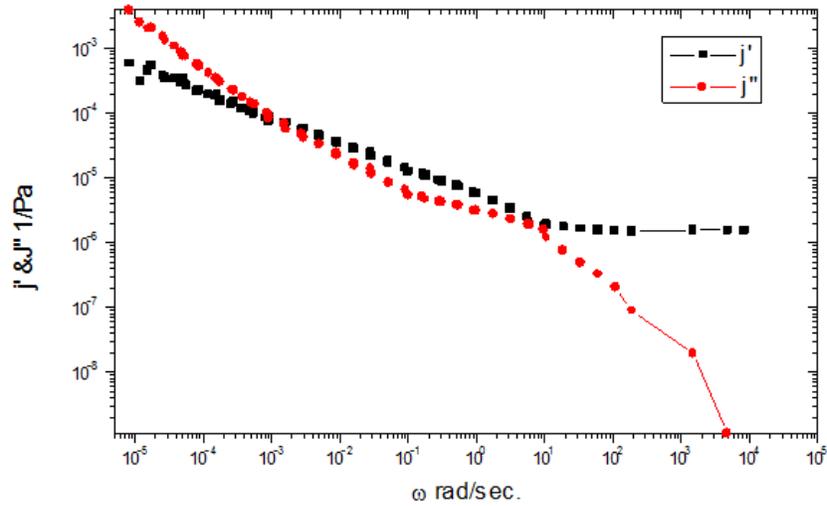
τ_i : the relaxation time

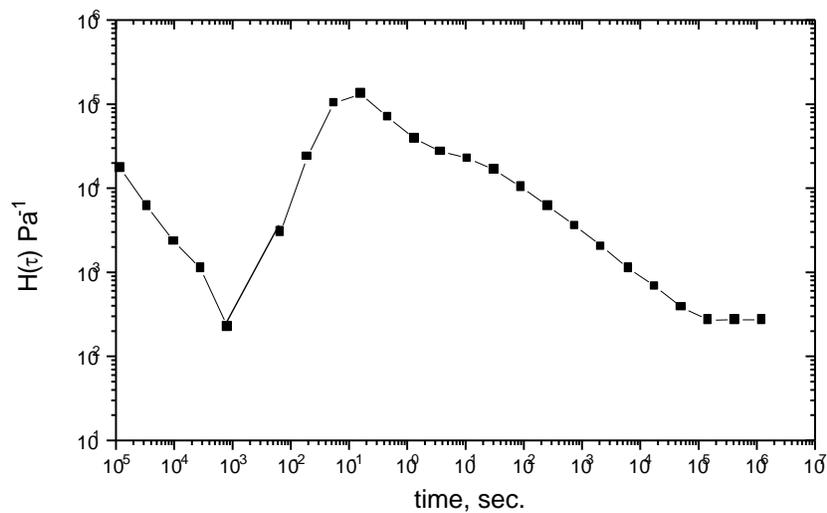*Figure 1: Master curve of the compliance for PVA 83K at T_0 =25C.*

Figure 2: Plot of the relaxation spectrum for PVA 83K at T_0 =25C.